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Laerdahl, J.K.; Fægri jr., K.; Visscher, L.; Saue, T.

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# A fully relativistic Dirac–Hartree–Fock and second-order Møller–Plesset study of the lanthanide and actinide contraction

J. K. Laerdahl[a] and K. Fægri, Jr.
*Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*

L. Visscher
*Department of Chemistry, University of Odense, Campusvej 55, DK-5230 Odense, Denmark*

T. Saue
*IRSAMC-LPQ, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse, France*

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Fully relativistic four-component self-consistent field and correlated calculations at the Møller–Plesset second-order perturbation theory level (MP2) have been performed for the monofluorides and mono- and trihydrides of lanthanum, lutetium, actinium, and lawrencium. The calculated spectroscopic constants are in good agreement with available experimental data. The calculated bond lengths have been compared with values from nonrelativistic calculations to give an estimate of the effect of relativity on the molecular lanthanide and actinide contraction. The calculated lanthanide contraction at the relativistic MP2 level is 0.12, 0.12, and 0.19 Å for the monohydrides, monofluorides, and trihydrides, respectively. The corresponding results for the actinides are 0.20, 0.15, and 0.28 Å, and we demonstrate that the larger size of the actinide contraction is a consequence of relativistic effects. Between 10% and 30% of the lanthanide contraction and between 40% and 50% of the actinide contraction is caused by relativity in these compounds.  [S0021-9606(98)30348-7]

## I. INTRODUCTION

The filling up of the $4f$ orbitals through the lanthanide series from lanthanum to lutetium is accompanied by a steady decrease of the atomic and ionic size. This explains why the atoms or ions of the same group in the second and third transition series have almost the same size while the corresponding species in the first transition series are significantly smaller. A similar contraction is also observed across the actinide series from actinium to lawrencium, and the trends are called the lanthanide and actinide contraction respectively (e.g., Ref. 1). The usual textbook explanation is that the increased electrostatic attraction of the nucleus across the series is imperfectly screened by the concurrent addition of *f*-electrons, but it has also been shown that relativistic effects are important, especially for the actinide contraction.[2,3] The importance of relativity for actinide chemistry is well-known,[4] and its importance also for the lanthanide contraction has within the past ten years been recognized in textbooks in inorganic chemistry.[1]

The lanthanide and actinide contractions may be illustrated by comparing the ionic sizes of the elements along the $4f$- and $5f$-blocks. The ionic radii given by Shannon[5] for the $Me^{3+}$ lanthanide ions with coordination number six may be used to calculate a lanthanide contraction, $\Delta_{Ln}=0.17$ Å from the simple difference

$$\Delta_{Ln}=R(La^{3+})-R(Lu^{3+}), \tag{1}$$

where the ions have the configurations $[Xe]$ and $[Xe]4f^{14}$ for $La^{3+}$ and $Lu^{3+}$, respectively. As the only difference between the ions is the increased nuclear charge and the 14 electrons that fill the $4f$-shell this provides a direct measure of the contraction. This procedure gives slightly different values for the contraction if other ionic charges or coordination numbers are used for lanthanum and lutetium, and the values are also dependent on the somewhat arbitrary definition of the ionic and atomic radius which cannot be observed directly experimentally. Due to the lack of experimental data for lawrencium the experimental actinide contraction, $\Delta_{An}$, is not well determined. From the ionic radii estimated by David *et al.*[6] an actinide contraction of 0.18 Å may be calculated. Küchle *et al.*[2] have argued that a more reasonable value is 0.22 Å, slightly larger than the value of 0.17 Å for the lanthanide ions of the same type.

The contraction of atomic orbitals across the lanthanide and actinide series has also been used as a measure of the lanthanide and actinide contraction. The position of the maximum of the electron radial distribution function $r_{max}$ and the radial expectation values $\langle r\rangle$ for different orbitals have been determined in atomic *ab initio* calculations. This might give more accurate values than the experimental results for the actinide contraction, due to the scarcity of experimental material available for the last several elements in the $5f$-block. *Ab initio* calculations may also be used to investigate the correctness of different models and explanations for the contractions. One may, for example, investigate to what degree the usual explanation of the increased effective nuclear charge is appropriate, or if relativity has any influence on the contractions by comparing relativistic and

[a]Current address: Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand.

 

nonrelativistic calculations. From the relativistic Dirac–Hartree–Fock (DHF) reference data of Desclaux[7] we can, for example, calculate a contraction of both $r_{\max}$ and $\langle r \rangle$ of $\sim 0.2$ Å for the $5p$-spinors from lanthanum to lutetium. Dolg and Stoll[8] have summarized the results for a number of DHF and nonrelativistic Hartree–Fock (HF) calculations and find that the results depend quite strongly on the atomic or ionic state and the orbital for which $r_{\max}$ or $\langle r \rangle$ is calculated. However, the most serious problem with these values is the neglect of electron correlation in the models. One would expect that since most systems both have many low-lying excited states and a large number of valence electrons both nondynamical and dynamical correlation will be important for the $4f$- and $5f$-block atoms and ions.

The ionic radii as well as $r_{\max}$ and $\langle r \rangle$ cannot be measured directly by experiment. Pyykkö[9] was the first to investigate the lanthanide and actinide contraction by calculating the parameters

$$\Delta_{\mathrm{Ln}} = r_e(\mathrm{LaH}) - r_e(\mathrm{LuH}),$$
$$\Delta_{\mathrm{An}} = r_e(\mathrm{AcH}) - r_e(\mathrm{LrH}), \tag{2}$$

where the accuracy of the calculated bond lengths may be tested by comparing with experimental values. Pyykkö performed Dirac–Hartree–Fock one-center calculations for the monohydrides and found molecular lanthanide and actinide contractions of 0.21 and 0.33 Å, respectively, and small but significant relativistic effects for the lanthanide contraction.

Two recent calculations have shown that these estimates for the contractions are too high due to the limitations of the one-center approximation and the neglect of electron correlation. The structure of the lanthanum and lutetium monohydrides, monofluorides, and monoxides were determined by nonrelativistic and quasirelativistic density functional theory (DFT) by Wang and Schwarz[10] and in high quality correlated pseudopotential calculations by Küchle *et al.*[2] New estimates for the molecular lanthanide contraction were obtained together with an estimate of the influence of relativity. In Ref. 2 the corresponding actinium and lawrencium compounds were also studied, and values for the actinide contraction were determined.

Küchle *et al.*[2] performed pseudopotential calculations with extensive valence basis sets for these heavy systems, and they have treated correlation at a high level of theory by performing coupled cluster calculations [CCSD and CCSD(T)] and multireference averaged coupled-pair functional (MRACPF) calculations. Their results are in good agreement with the available experimental data and do not vary between the formally single and multireference methods by more than a few picometers for bond lengths and a few percent for the force constants indicating that all these correlated methods give good results for the diatomic molecules. The main possible source of error in the calculations of Küchle *et al.*[2] is that relativity only is included through frozen core quasirelativistic pseudopotentials. Valence electrons are treated in a nonrelativistic formalism where these electrons are moving in the effective potential of the frozen core. The pseudopotential comprises the $(46+n)$ electron $[\mathrm{Kr}]4d^{10}4f^{n}$-core where $n=0$ for lanthanum and $n=14$ for lutetium and the actinides. Especially for lutetium the frozen core is rather large since the 14 valence $4f$ orbitals are included in the pseudopotential. These orbitals have energies higher than the valence electrons in the $5s$ and $5p$ orbitals, but are often described as ''inner-valence'' electrons since they are more radially contracted. Even if it has been demonstrated in many earlier studies that pseudopotential calculations give good results for spectroscopic properties of molecules containing heavy elements, fully relativistic methods are necessary to give benchmarks from which the quality of the less accurate methods may be determined.

In this work fully relativistic four-component self-consistent field (SCF) calculations and correlated calculations at the Møller–Plesset second-order perturbation theory level (MP2) have been performed to study the lanthanide and actinide contraction. The formalism and techniques of Dirac–Hartree–Fock (DHF) SCF calculations are described in e.g., Refs. 11–13. Single particle relativistic effects have been accounted for by the Dirac Hamiltonian, but the electron–electron interaction has been described by the instantaneous Coulomb interaction. Many-particle relativistic effects are known to have little influence on the spectroscopic constants considered here (e.g., Ref. 14), justifying the neglect of the Breit term and higher order radiative corrections. Prior to this work a new version of the relativistic MP2 (RMP2) program of Laerdahl *et al.*[15] has been developed. It is similar to scheme 2 of Ref. 15, but molecular point group symmetry is exploited to simplify and seriously reduce the computational cost involved. Both the DHF and RMP2 codes use direct algorithms for the calculation of two-electron integrals and are built into the DIRAC program system.[11]

After a short summary of the details of the calculations in Sec. II we present and discuss the results in Sec. III. The results are furthermore compared with nonrelativistic HF and MP2 calculations to obtain values for the effect of relativity on the lanthanide and actinide contractions. These results are summarized in Sec. IV where we also argue that fully relativistic calculations no longer are prohibitively expensive compared with nonrelativistic calculations.

## II. COMPUTATIONAL DETAILS

Gaussian basis sets of dual-family type were generated for lanthanum, lutetium, actinium, and lawrencium using a version of the atomic program GRASP[16] modified for basis set calculations.[12] Recently a basis set optimization module has also been included in the program.[17] The optimization of the basis sets is summarized in the Appendix. The ligand atoms were described by Dunning's correlation-consistent polarized triple-zeta basis sets (cc-pVTZ).[18] For hydrogen the primitive $5s2p1d$ cc-pVTZ basis set was augmented with one diffuse $s$ and $p$ function.[19] The fluorine atom was described by the $10s5p2d1f$ cc-pVTZ basis set and augmented with one diffuse $s$, $p$, and $d$ function.[19] All the Gaussian basis sets have been used in spherical and uncontracted form for the large component functions, and the small component basis sets were generated from the large component sets using a linear transformation and a projection[20] that is equivalent to the restricted kinetic balance (RKB) condition.[13,21] Within

TABLE I. Nonrelativistic (NR) and relativistic (R) SCF and MP2 bond lengths ($r_e$) for the lanthanum and lutetium compounds. The molecular lanthanide contraction is calculated from $\Delta_{\mathrm{Ln}}=r_e(\mathrm{LaX}_x)-r_e(\mathrm{LuX}_x)$. An estimate of the basis set superposition error (BSSE) is given by the counterpoise corrected (Ref. 26) bond lengths given in parentheses for the diatomic molecules. All the valence electrons have been correlated in the MP2 calculations. However, we also tested the effect of not correlating the inner-valence $4f$-electrons in the lutetium compounds (Ref. 1). For LaH and LuH the results for the calculations where the subvalence electrons also are correlated are given. The experimental values (Exp.) are taken from Huber and Herzberg (Ref. 25), except for the results for LaH (Ref. 28) and LaF (Ref. 36).

| | | Number of electrons correlated | $r_e$ (Å) (NR) | $r_e$ (Å) (R) |
|---|---|---|---|---|
| LaH ($^1\Sigma^+$) | | | | |
| | SCF | | 2.032 | 2.053 |
| | MP2 | 12 | 1.982 (1.996) | 2.005 |
| | MP2 | 30 | 1.980 (1.996) | 2.006 |
| | Exp. | | | 2.032 |
| LuH ($^1\Sigma^+$) | | | | |
| | SCF | | 1.936 | 1.958 |
| | MP2 | 12[a] | | 1.923 |
| | MP2 | 26 | 1.872 (1.883) | 1.882 |
| | MP2 | 44 | 1.874 (1.886) | 1.883 |
| | Exp. | | | 1.912 |
| $\Delta_{\mathrm{Ln}}$(LnH) | | | | |
| | SCF | | 0.096 | 0.095 |
| | MP2 | 12[a] | | 0.082 |
| | MP2 | 12(+14) | 0.110 (0.113) | 0.123 |
| | MP2 | 30(+14) | 0.106 (0.110) | 0.123 |
| | Exp. | | | 0.120 |
| LaF ($^1\Sigma^+$) | | | | |
| | SCF | | 2.045 | 2.054 |
| | MP2 | 18 | 2.026 (2.035) | 2.038 |
| | Exp. | | | 2.026 |
| LuF ($^1\Sigma^+$) | | | | |
| | SCF | | 1.952 | 1.945 |
| | MP2 | 18[a] | | 1.953 |
| | MP2 | 32 | 1.926 (1.933) | 1.916 |
| | Exp. | | | 1.917 |
| $\Delta_{\mathrm{Ln}}$(LnF) | | | | |
| | SCF | | 0.093 | 0.109 |
| | MP2 | 18[a] | | 0.085 |
| | MP2 | 18(+14) | 0.100 (0.102) | 0.122 |
| | Exp. | | | 0.109 |
| $LaH_3$ ($^1A_1$), ($D_{3h}$)[b] | | | | |
| | SCF | | 2.146 | 2.162 |
| | MP2 | 14 | 2.090 | 2.111 |
| $LuH_3$ ($^1A_1$), ($D_{3h}$)[b] | | | | |
| | SCF | | 2.013 | 1.985 |
| | MP2 | 14[a] | | 1.954 |
| | MP2 | 28 | 1.954 | 1.922 |
| $\Delta_{\mathrm{Ln}}(\mathrm{LnH_3})$ | | | | |
| | SCF | | 0.133 | 0.177 |
| | MP2 | 14[a] | | 0.157 |
| | MP2 | 14(+14) | 0.136 | 0.189 |

[a]The 14 subvalence $4f$-electrons were not correlated in these calculations on lutetium compounds.

[b]The structure of the $LaH_3$ and $LuH_3$ molecules were optimized with a $D_{3h}$ symmetry constraint.

this scheme the scalar basis sets used to expand the molecular four-spinors are equivalent to RKB two-spinor basis sets of $N_{2\mathrm{spin}}$ large component functions and the same number of small component functions. In this work the number of scalar basis functions have been between 869 and 1218 for the molecules that we have studied. This corresponds to values for $N_{2\mathrm{spin}}$ between 250 and 350. $N_{2\mathrm{spin}}$ is also the number of spherical basis functions in the nonrelativistic calculations for each molecule.

The GAUSSIAN 94[22] and DALTON[23] program systems were used for the nonrelativistic SCF and MP2 calculations. In the relativistic calculations the Kramers-restricted, DHF closed-shell wavefunctions were generated in the DIRAC[11] program with a direct SCF algorithm. Finite size Gaussian nuclei were used, and the nuclear exponents were taken from the list of values recommended by Visscher and Dyall.[24]

In both the relativistic and nonrelativistic MP2 calculations the active virtual space for correlation was restricted to orbitals with energies less than 100 a.u., a simplification which is expected to have a negligible effect on the calculated properties. All the valence electrons were correlated, but experiments were also performed to investigate the error introduced by not correlating the subvalence electrons. For lutetium we performed calculations to test the effect of not correlating the 14 inner-valence $4f$-electrons as well. In the DHF calculations all integral classes were included, but in all the RMP2 calculations the $(LL|LL)$ and $(SS|LL)$ type integrals were included in the energy expression while the $(SS|SS)$ integrals were neglected. Here $L$ is a large component and $S$ a small component basis function.[15] The effect of neglecting the $(SS|SS)$ integrals in the RMP2 calculations was tested for LrH. When the $(SS|SS)$ integrals were included in the RMP2 energy expression the potential-energy curve was shifted down by $9.2\times10^{-6}$ a.u., but this had no effect on the calculated spectroscopic constants. This is in agreement with the results for the AgF and AuF molecules in Ref. 15 and confirms that the $(SS|SS)$ integrals may safely be neglected in the calculation of the RMP2 energy in investigations of valence properties. The cost of the RMP2 calculation is then lowered by a factor of between 2 and 3.

Geometry optimization was carried out through stepwise variation of the metal–ligand bond distance. The energy was calculated at several bond lengths around the equilibrium ($r_e$), and force constants were calculated by a quadratic fit to three points at exactly $r=r_e$ and $r=r_e\pm0.01$ Å. The vibrational frequencies were calculated from the force constants and the reduced masses listed by Huber and Herzberg.[25] All the $MeH_3$ molecules were geometry optimized with a $D_{3h}$ symmetry constraint, and only the Me–H bond distance was optimized. However, at the nonrelativistic level a full optimization of the geometry was performed for $LaH_3$ and $LuH_3$. The effect of basis set superposition error (BSSE) was investigated by the counterpoise correction method[26] at the nonrelativistic MP2 level for the diatomic lanthanide compounds.

## III. RESULTS AND DISCUSSION

### A. Accuracy of the calculations

#### 1. Electronic states and nondynamical correlation

The main purpose of this work is to investigate the influence of relativity on the lanthanide and actinide contractions, and we have consequently only performed closed-shell calculations on the lowest lying $^1\Sigma^+$ state for the lanthanum, lutetium, actinium, and lawrencium monohydrides and

TABLE II. Nonrelativistic (NR) and relativistic (R) SCF and MP2 force constants and vibrational frequencies for the diatomic lanthanum and lutetium compounds. An estimate of the basis set superposition error (BSSE) is given by the counterpoise corrected (Ref. 26) force constants in parentheses. See Table I for an explanation of the active electrons in the MP2 calculations. The experimental values (Exp.) are taken from Huber and Herzberg (Ref. 25) and the force constants and vibrational frequencies are related through the reduced masses *ibid.* No experimental data is available for the LaH vibrational frequency.

| | | Number of electrons correlated | $k_e$ ($Nm^{-1}$) (NR) | $k_e$ ($Nm^{-1}$) (R) | $\omega_e$ ($cm^{-1}$) (NR) | $\omega_e$ ($cm^{-1}$) (R) |
|---|---|---|---|---|---|---|
| LaH | | | | | | |
| | SCF | | 114 | 122 | $1.39\times10^3$ | $1.44\times10^3$ |
| | MP2 | 12 | 126 (124) | 131 | $1.46\times10^3$ | $1.49\times10^3$ |
| | MP2 | 30 | 129 (127) | 132 | $1.48\times10^3$ | $1.50\times10^3$ |
| | Exp. | | | | | |
| LuH | | | | | | |
| | SCF | | 140 | 130 | $1.54\times10^3$ | $1.48\times10^3$ |
| | MP2 | 12[a] | | 136 | | $1.52\times10^3$ |
| | MP2 | 26 | 151 (150) | 141 | $1.60\times10^3$ | $1.54\times10^3$ |
| | MP2 | 44 | 151 (150) | 141 | $1.60\times10^3$ | $1.54\times10^3$ |
| | Exp. | | | | | 1520 |
| LaF | | | | | | |
| | SCF | | 292 | 308 | 545 | 559 |
| | MP2 | 18 | 314 (306) | 321 | 565 | 571 |
| | Exp. | | | | | 570 |
| LuF | | | | | | |
| | SCF | | 370 | 358 | 606 | 596 |
| | MP2 | 18[a] | | 370 | | 606 |
| | MP2 | 32 | 384 (386) | 368 | 616 | 604 |
| | Exp. | | 612 | | | |

[a]The 14 subvalence $4f$-electrons were not correlated in these calculations on lutetium compounds.

monofluorides and $^1A_1$ state for the trihydrides. For all the diatomic lanthanide compounds investigated here $^1\Sigma^+$ appears to be the ground state. It is well known that LuH and LuF both have $^1\Sigma^+$ ground states,[25] but there has been some confusion with respect to the ground state of LaF and LaH. However, Schall *et al.*[27] established the $^1\Sigma^+$ ground state of LaF, and Ram and Bernath[28] recently reinvestigated the LaH and LaD spectrum and concluded that also LaH has a $^1\Sigma^+$ ground state, in agreement with theoretical results of Das and Balasubramanian.[29] It is not known to the authors that there are any gas-phase experimental data available for any of the actinide compounds that we have studied in this work, but from the similar appearance of the electron configuration and bonding for the lanthanide and actinide compounds we conclude that the $^1\Sigma^+$ state is the ground state or at least a low-lying state for the actinide monohydrides and monofluorides. All the trihydrides appear to be stable closed-shell molecules, but the authors are not aware of any experimental studies of these compounds. The calculated bond lengths, force constants and vibrational frequencies from the nonrelativistic and fully relativistic four-component SCF and MP2 calculations are given in Tables I and II for the lanthanide compounds, where also the available experimental data is presented. The corresponding results for the hydrides and monofluoride of actinum and lawrencium are given in Tables III and IV.

The ground-state electron configuration of lanthanum and lutetium may be written as $[\mathrm{Ar}]3d^{10}4s^24p^6 4d^{10}5s^25p^64f^m\ 6s^25d^1$ where $m=0$ for lanthanum and $m=14$ for lutetium. We will call $[\mathrm{Ar}]3d^{10}$ the core, the 18 $4s$, $4p$, and $4d$ electrons the subvalence, and the remaining

TABLE III. Nonrelativistic (NR) and relativistic (R) SCF and MP2 bond lengths ($r_e$) for the actinium and lawrencium compounds. The molecular actinide contraction is calculated from $\Delta_{\mathrm{An}}=r_e(\mathrm{AcX}_x)-r_e(\mathrm{LrX}_x)$. All the valence electrons were correlated in the MP2 calculations.

| | | Number of electrons correlated | $r_e$ (Å) (NR) | $r_e$ (Å) (R) |
|---|---|---|---|---|
| AcH ($^1\Sigma^+$) | | | | |
| | SCF | | 2.104 | 2.183 |
| | MP2 | 12 | 2.050 | 2.129 |
| LrH ($^1\Sigma^+$) | | | | |
| | SCF | | 1.986 | 2.008 |
| | MP2 | 26 | 1.928 | 1.925 |
| $\Delta_{\mathrm{An}}$(AnH) | | | | |
| | SCF | | 0.118 | 0.175 |
| | MP2 | 12(+14) | 0.122 | 0.204 |
| AcF ($^1\Sigma^+$) | | | | |
| | SCF | | 2.104 | 2.142 |
| | MP2 | 18 | 2.088 | 2.131 |
| LrF ($^1\Sigma^+$) | | | | |
| | SCF | | 2.033 | 2.011 |
| | MP2 | 32 | 2.010 | 1.985 |
| $\Delta_{\mathrm{An}}$(AnF) | | | | |
| | SCF | | 0.071 | 0.131 |
| | MP2 | 18(+14) | 0.078 | 0.146 |
| $AcH_3$ ($^1A_1$), ($D_{3h}$)[a] | | | | |
| | SCF | | 2.225 | 2.264 |
| | MP2 | 14 | 2.164 | 2.215 |
| $LrH_3$ ($^1A_1$), ($D_{3h}$)[a] | | | | |
| | SCF | | 2.085 | 2.004 |
| | MP2 | 28 | 2.024 | 1.934 |
| $\Delta_{\mathrm{An}}(\mathrm{AnH_3})$ | | | | |
| | SCF | | 0.140 | 0.260 |
| | MP2 | 14(+14) | 0.140 | 0.281 |

[a]The structure of the $AcH_3$ and $LrH_3$ molecules were optimized with a $D_{3h}$ symmetry constraint.

TABLE IV. Nonrelativistic (NR) and relativistic (R) SCF and MP2 force constants for the diatomic actinium and lawrencium compounds. All the valence electrons were correlated in the MP2 calculations.

| | Number of electrons correlated | $k_e$ ($\mathrm{Nm}^{-1}$) (NR) | $k_e$ ($\mathrm{Nm}^{-1}$) (R) |
|---|---|---|---|
| AcH | | | |
| SCF | | 104 | 108 |
| MP2 | 12 | 117 | 116 |
| LrH | | | |
| SCF | | 133 | 116 |
| MP2 | 26 | 144 | 127 |
| AcF | | | |
| SCF | | 267 | 281 |
| MP2 | 18 | 290 | 285 |
| LrF | | | |
| SCF | | 342 | 322 |
| MP2 | 32 | 361 | 333 |

$(11+m)$ electrons are the valence electrons. Mainly the $6s$ and $5d$ orbitals are involved in the bonding, and we tentatively write the bonding as $\sigma_1^2\sigma_2^2$ for LnH and $(\mathrm{F},2p_{\sigma_1})^2(\mathrm{F},2p_{\pi})^4\sigma_2^2$ for the ionic model of LnF. In both the hydride and fluoride the Ln $6s$ orbital gives the main contribution to the $\sigma_2$ orbital. Similar models can be used to describe also the trihydrides and the actinide compounds. One should note, however, that many molecules containing *f*-block elements may only be described accurately by a multireference calculation, so that a single reference state as given by the electron configurations above might not be a good description of the system. We do not expect the degree of multireference character of the system to be much influenced by relativity for the molecules studied in this work, and we have calculated the nonrelativistic MP2 natural orbital (NO) occupation numbers for the systems.[30] In all the diatomic lanthanide (actinide) compounds the $6s$- ($7s$-)like $\sigma_2$ orbital has a MP2 NO occupation number between 1.91 and 1.93, but all other occupied orbitals have values larger than 1.95 indicating that the multireference character will not be very serious for these compounds. Currently an efficient four-component relativistic multireference SCF program is not available, and relativistic multireference configuration interaction (CI) calculations for this system would be prohibitively expensive if we should retain the same large active spaces and basis sets. For smaller basis sets or active spaces the accuracy would probably be lower than obtained with the current single reference approach, and also earlier nonrelativistic and quasirelativistic calculations indicate that the errors introduced in the calculated spectroscopic constants by neglecting the multireference character of the systems are small. An example is the work of Küchle *et al.*[2] where the formally single reference CCSD method gives results very similar to the multireference MRACPF method for all the diatomic systems we are considering in this work. Bond lengths calculated by the two methods differ by at most 0.014 Å and force constants by less than 5%. From earlier experience we do, however, expect the MP2 method to have larger problems with multireference systems than the CCSD method, and this must be taken into account in the analysis of the calculated properties. All the trihydrides have MP2 NO occupation numbers larger than 1.95 for the occupied orbitals and are accurately described by a single reference state.

The valence basis sets of Küchle *et al.*[2] are of a quality comparable to our basis sets. For all the diatomic compounds our nonrelativistic SCF properties deviate by no more than 0.01 Å for bond lengths and 3% for the force constants from those of Ref. 2. Since Küchle *et al.*[2] included correlation at a higher level of theory than the MP2 calculations in this work we may test the accuracy of our MP2 calculations by comparing our results for the diatomic molecules with the correlated single and multireference calculations of Ref. 2. An agreement between our results, the pseudopotential calculations and experiment would indicate both that the less expensive treatment of relativity in the pseudopotential calculations as well as the MP2 treatment in our calculations are justified.

### 2. Basis set superposition error

In the recent work of Küchle *et al.*[2] basis set superposition error (BSSE) was found to be very significant in pseudopotential calculations on the monohydrides, monofluorides, and monoxides of lanthanum and lutetium with valence basis sets of accuracy comparable to our basis sets. BSSE was not important at the SCF level, but for the correlated calculations the BSSE accounts for up to 0.04 Å on bond lengths and 5% to 10% on force constants. It is possible to give an estimate of the BSSE by the counterpoise correction method[26] where the energies for the fragments of the system are calculated in the basis set of the full molecule. The counterpoise correction method requires open shell calculations, and as we do not have a program available for relativistic open shell calculations we are unable to investigate the effect of BSSE in the relativistic case. We do, however, not expect the BSSE to be significantly influenced by relativity, and have calculated nonrelativistic counterpoise corrected values for the bond lengths and force constants for the diatomic lanthanide molecules. The values are given together with the uncorrected results in Tables I and II, and shows that the effect is largest for LaH yielding a 0.016 Å bond contraction and a 2 $\mathrm{Nm}^{-1}$ (2%) increase of the force constant from BSSE. This is in reasonable agreement with the results of Küchle *et al.*[2] for the actinide monohydrides and monofluorides and indicates that the large BSSE found in Ref. 2 for the lanthanide compounds is connected with the large frozen core in these pseudopotential calculations or possibly with a basis set deficiency. The BSSE for calculations with a small frozen core, such as the actinide compound calculations of Ref. 2 appears to be comparable to the calculations presented here which do not have a frozen core. From these results we estimate that the effect of BSSE in all our relativistic and nonrelativistic calculations will be that the calculated bond lengths are between 0.005 and 0.018 Å too short. The force constants and vibrational frequencies similarly have errors of a few percent due to BSSE.

### 3. Correlation space

In correlated calculations of valence properties it is usually not necessary to correlate the core electrons since this

only gives a vertical shift of the potential-energy surface and has a negligible effect on bond lengths, force constants and dissociation energies. We have investigated the error introduced by not correlating the 18 subvalence electrons that mainly have contributions from the *ns*, *np*, and *nd* atomic orbitals where $n=4$ for the lanthanides and $n=5$ for the actinides. The results for the lanthanide monohydrides are given in Tables I and II. We also performed these experiments for the other lanthanide compounds at the nonrelativistic MP2 level. The largest errors were 0.002 Å for bond lengths and 3% for the force constants. In nonrelativistic MP2 calculations on the actinide compounds we found slightly larger errors when the subvalence electrons not were correlated. The largest errors were 0.004 and 0.006 Å for the AcH and $AcH_3$ bond lengths and 3% for the AcF and AcH force constants. In summary the errors introduced by not correlating the subvalence electrons are significantly less than 0.01 Å for the bond lengths for all the molecules and only a few percent for force constants, and due to the heavy computational demands of using large active spaces we have correlated only the valence electrons in all the remaining RMP2 calculations. Experiments on not correlating the inner-valence $4f$-electrons in the lutetium compounds have also been performed, but only at the relativistic level since our nonrelativistic codes do not have the flexibility that allow us to perform these experiments. Tables I and II clearly show, however, that it is necessary to correlate the inner-valence $4f$-electrons to obtain correct results for the electron correlation.

#### 4. Symmetry restrictions

Earlier experimental work and calculations on lanthanum trihydrides[31] and on lanthanide trihalides (e.g., Ref. 8) have all found ground-state geometries with $D_{3h}$ or $C_{3v}$ symmetry. In all cases where the minimum is of the $C_{3v}$ type the inversion barrier of the molecule is of the order of a few kcal/mol or less, and the change in bond length between the $C_{3v}$ minimum and the $D_{3h}$ saddle point is small. For reasons of economy we have only optimized the geometries with a $D_{3h}$ symmetry constraint in the relativistic calculations and in the calculations on the actinide trihydrides. For the lanthanide trihydrides we performed the full geometry optimization at the nonrelativistic SCF and MP2 level, and the results are given in Table V. $LaH_3$ has a $C_{3v}$ minimum with inversion barriers of 0.25 and 0.86 kcal/mol at the SCF and MP2 level, respectively. $LuH_3$ has a $D_{3h}$ minimum at the SCF level, but at the MP2 level the $C_{3v}$ configuration has a slightly lower energy. We are here mainly interested in the effect of relativity on the lanthanide and actinide contraction, and we do not expect the calculated relativistic effects at the $D_{3h}$ saddle point to be significantly different from the relativistic effects calculated from the global minimum molecular configurations. We expect this also to be the case for the $AcH_3$ and $LrH_3$ molecules. There is, however, a problem with the definition of the total lanthanide contractions since the bond lengths in $LaH_3$ change by as much as 0.01 Å from the $C_{3v}$ to the $D_{3h}$ geometry, resulting in an uncertainty of this magnitude in the contractions calculated at the $D_{3h}$ geometry. We cannot report force constants for the trihydrides since we have not performed the full geometry optimizations.

TABLE V. Nonrelativistic geometries at the SCF and MP2 level for the full optimization ($C_{3v}$) and optimization with a $D_{3h}$ symmetry constraint for $LaH_3$ and $LuH_3$. All valence electrons were correlated in the MP2 calculations. Optimized bond lengths ($r_e$), H–Ln–H bond angles ($\varphi$) and the inversion barrier of the molecule ($\Delta E$) are given in the table. The $D_{3h}$ geometry is the global minimum for $LuH_3$ at the SCF level.

| | | $r_e$ (Å) | $\varphi$ | $\Delta E$ (kcal/mol) |
|---|---|---|---|---|
| $LaH_3$ (SCF) | $C_{3v}$ | 2.139 | 116.8° | 0 |
| | $D_{3h}$ | 2.146 | 120.0° | 0.25 |
| $LaH_3$ (MP2) | $C_{3v}$ | 2.081 | 113.8° | 0 |
| | $D_{3h}$ | 2.090 | 120.0° | 0.86 |
| $LuH_3$ (SCF) | $C_{3v}$ | 2.013 | 120.0° | 0 |
| $LuH_3$ (MP2) | $C_{3v}$ | 1.953 | 119.3° | 0 |
| | $D_{3h}$ | 1.954 | 120.0° | $9.4\times10^{-3}$ |

### B. Lanthanide compounds

We define the relativistic effect on the bond lengths by $\Delta_R r_e = r_e^R - r_e^{NR}$. It is seen from Table I that $\Delta_R r_e$ is small for all the lanthanide compounds we have studied. The absolute value of the effect is always less than 0.03 Å, with small relativistic bond contractions for $LuH_3$ and LuF and small expansions for LaH, LuH, LaF, and $LaH_3$. For all the molecules the correlation effects are more significant than relativistic effects, contracting the bonds between 0.05 and 0.08 Å for the hydrides and between 0.01 and 0.03 Å for the fluorides. The smaller effect of correlation for the fluorides is presumably caused by the more rigid bonds in these compounds. Taking into account the quality of the basis sets and the limitations of the RMP2 method it is seen that the calculated bond lengths at the RMP2 level are in good agreement with the available experimental data. For LaH and LuH the calculated bond lengths are 0.026 and 0.029 Å too short, and the RMP2 method is seen to ''overshoot'' and give too short bond lengths, whereas the DHF results give too long bond lengths. The RMP2 results for the diatomic fluorides are in even better agreement with experiment. Note that the large number of *f*-type polarization functions for lanthanum in Table X is necessary to give an accurate description of the bonding. If the four inner *f*-functions are excluded from the basis set the bond lengths expand by as much as 0.03 Å for some of the lanthanum compounds. This is an indication that the $4f$ orbitals are involved in the bonding in these systems.

The calculated RMP2 harmonic force constants and vibrational frequencies in Table II are in excellent agreement with experiment, and errors are only slightly larger than 1% compared with the available experimental data for LuH, LaF, and LuF. Correlation increases all the force constants by 10 to 15 $Nm^{-1}$ in agreement with the rule that bond shortening is accompanied by an increase in the force constants (e.g., Ref. 32).

If we compare the MP2 nonrelativistic BSSE corrected values in our work with the correlated calculations in Ref. 2 we obtain differences of 0.044 and 0.006 Å for LaH and LaF, respectively. The large difference for LaH may be due

to a shortfall of the MP2 method. However, the excellent agreement between the MP2 and CCSD results for the actinide compounds (Sec. III C) indicates that the difference is due to a basis set deficiency in Ref. 2. The BSSE of 0.04 Å is very large for LaH in that study as well. Our nonrelativistic calculations for LuH and LuF are not directly comparable with the results of Küchle *et al.*[2] since they have excluded the inner-valence $4f$-electrons from the active valence space. We obtain bond contractions due to correlation at the RMP2 level of 0.08 Å for LuH and 0.03 Å for LuF, values that perhaps should be reduced by about 0.01 Å to correct for BSSE. However, if we do not correlate the $4f$-electrons in the RMP2 calculations, these values change to 0.04 and $-0.01$ Å for LuH and LuF, respectively, in reasonable agreement with the CCSD results of Ref. 2. It does appear that including the $4f$-electrons in the inactive core removes that flexibility of the $4f$-shell to relax upon correlation giving a significant underestimation of the correlation effect on the bonding. Our results in Table I indicate that for LuH and $LuH_3$ only about 50% of the bond contraction due to correlation is obtained if the $4f$-electrons are not correlated. For LuF the effect is even more dramatic giving a small bond expansion upon correlation, and only when the $4f$-electrons are correlated, the more correct contraction of 0.03 Å is obtained. Some of the core-valence correlation may be obtained by using core-polarization potentials in the pseudopotential calculations. Core-polarization potentials for the *f*-block elements have been generated by Wang and Dolg.[33] These give pseudopotential results that are in better agreement with ours for the lutetium compounds and reduce the bond lengths with as much as a few pm at the correlated level.[34]

### C. Actinide compounds

The calculated bond lengths for the hydrides and monofluoride of the heavy elements actinium and lawrencium are given in Table III. As expected, the effect of relativity is larger than for the corresponding lanthanide compounds, but there are similar trends for the $4f$- and $5f$-block elements. In analogy with the lanthanide compounds it is only the trihydride and fluoride of the heaviest of the two elements that undergo any significant bond contraction due to relativity; 0.09 Å for $LrH_3$ and 0.03 Å for LrF at the MP2 level. At the correlated level there is almost no $\Delta_R r_e$ for LrH and bond expansions for all the actinide compounds; ~0.04 Å for AcF and $AcH_3$ and 0.08 Å for AcH. The nonadditivity of correlation and relativistic effects is small but significant, giving changes of $\Delta_R r_e$ from 0.01 to 0.02 Å between the SCF and MP2 calculations. The actinide compounds follow the same trends upon correlation as the lanthanide compounds. The MP2 calculations give a contraction of the bonds for all the hydrides between 0.05 and 0.08 Å. In analogy with the lanthanides, the fluorides experience a smaller contraction of between 0.01 and 0.03 Å.

It is not known to us that there are experimental data available for any of the actinide compounds, but we do not expect the calculated values to have larger errors than for the lanthanide compounds. The force constants for the monohydrides and monofluorides are given in Table IV. The AcH bond strength is hardly influenced by relativity, and AcF, LrH, and LrF all show weaker bonds when relativity is taken into account. There is, however, a significant nonadditivity of relativity and correlation effects. For the nonrelativistic calculations the MP2 correction strengthens the bonds by between 11 and 23 $Nm^{-1}$, whereas the corresponding strengthening of the bond for the relativistic calculations lies between 4 and 11 $Nm^{-1}$.

We expect the effect of BSSE to be similar for the diatomic actinides in this work and Ref. 2, and we may compare directly the uncorrected spectroscopic constants of Ref. 2 with our work. We find that the calculated properties for AcH, AcF, LrH, and LrF in Ref. 2 (without spin–orbit CI corrections) and this work are amazingly similar, with differences smaller than 0.02 Å for bond lengths and 11 $Nm^{-1}$ (~4%) for AcF and LrF as the largest difference in the force constants. These values are, however, of the same size as the difference between the SCF all-electron and pseudopotential calculations in Ref. 2, the effect of BSSE, and the effect of not correlating the subvalence electrons in the correlated calculations. We conclude that at least for these very heavy element compounds the quasirelativistic pseudopotential method is appropriate for the calculation of bond lengths and force constants at the relativistic level. Also the RMP2 method gives good results compared with a more accurate treatment of electron correlation and possible multireference problems do not seem to influence the results. Spin–orbit and correlation effects have been treated additively in Ref. 2, but the spin–orbit corrected results are in less agreement with our results where spin–orbit effects are included variationally.

It thus appears that we have the surprising result that the spectroscopic constants for the highly relativistic species AcH, AcF, LrH, and LrF are rather accurately described without spin–orbit coupling by the small core pseudopotential calculations in Ref. 2 where the valence electrons are treated nonrelativistically. However, even if the pseudopotential calculations with the large inactive core in lutetium give accurate results at the SCF level, the effect of correlation is severely underestimated due to the lack of flexibility for the $4f$-electrons. This will also have an effect on the estimated lanthanide contraction which will be discussed in the next section.

### D. Lanthanide and actinide contraction

The molecular lanthanide contraction $\Delta_{Ln}$ is given in Table I for the hydrides and the monofluoride that we have studied. Contrary to the early results of Pyykkö[9] relativity *reduces* the lanthanide contraction for the monohydrides by ~10% at the SCF level in Ref. 2. In our work the effect of relativity is negligible at the SCF level. However, at the MP2 level this is changed to an *increase* of ~10%, provided that the $4f$-electrons of lutetium are correlated. At the RMP2 level the calculated lanthanide contraction is in excellent agreement with the experimental value of 0.12 Å.

For the monofluorides the RMP2 $\Delta_{Ln}=0.12$ Å is in reasonable agreement with the experimental value (0.11 Å) and nearly identical to the result for the monohydrides. Approximately 15% of the MP2 lanthanide contraction for the monofluorides is a relativistic effect. The largest relativistic

TABLE VI. Radial expectation values (Å) for $(n-2)f^m(n-1)d^1ns^2$ electronic configurations of lanthanide and actinide atoms obtained from average level calculations using the atomic GRASP code (Ref. 16). Nonrelativistic values (in parentheses) have been obtained by scaling the speed of light with a factor of 2000.

| | La | Lu | $\Delta_{Ln}$ |
|---|---|---|---|
| $5d_{3/2}$ | 1.516 (1.459) | 1.426 (1.315) | 0.09 (0.14) |
| $5d_{5/2}$ | 1.540 (1.459) | 1.471 (1.315) | 0.07 (0.14) |
| $6s_{1/2}$ | 2.499 (2.610) | 2.065 (2.254) | 0.43 (0.36) |
| | Ac | Lr | $\Delta_{An}$ |
| $6d_{3/2}$ | 1.814 (1.623) | 1.631 (1.369) | 0.18 (0.25) |
| $6d_{5/2}$ | 1.882 (1.623) | 1.738 (1.369) | 0.14 (0.25) |
| $7s_{1/2}$ | 2.435 (2.770) | 1.945 (2.435) | 0.49 (0.33) |

effects are found for the trihydrides, where the total lanthanide contraction also is the largest; 0.19 Å for the RMP2 calculations. Both at the SCF and MP2 level relativity accounts for more than 25% of the lanthanide contraction for the trihydrides. The total nonrelativistic lanthanide contraction of ~0.135 Å is reduced by about 0.01 Å if the contraction is calculated as the difference in bond length between the minimum energy configurations of $LaH_3$ and $LuH_3$ in Table V. An uncertainty of the same size is also present in the relativistic case. Note that for all the three types of molecules it is necessary to correlate the $4f$-electrons in the lutetium compounds. If not, the effect of correlation will be a *decrease* in $\Delta_{Ln}$ instead of the correct *increase*. This seems to be the case for the calculations of Küchle *et al.*[2] where the large frozen core excludes the $4f$-electrons from the space that can be relaxed upon bonding. Some of this deficiency may be corrected with core-polarization potentials.[34]

The data for the actinide contraction $\Delta_{An}$ are given in Table III, where it can be seen that the relativistic effects are very important for all the molecules. The actinide contraction is approximately the same as the lanthanide contraction for the three types of molecules at the nonrelativistic level. However, at the relativistic level the actinide contraction for the hydrides increases by almost a factor of 2 giving a contraction that is at least 50% larger than $\Delta_{Ln}$ for the corresponding systems. For the fluorides the small nonrelativistic $\Delta_{An}$ is increased to a slightly larger value than the corresponding lanthanide contraction when relativity is included. In summary, relativity accounts for 40%, 47%, and 50% of the actinide contraction for the monohydrides, monofluorides, and trihydrides, respectively, giving a total contraction at the RMP2 level of 0.20 Å for the monohydrides, 0.15 Å for the monofluorides, and the largest contraction of 0.28 Å for the trihydrides. The results for the diatomic molecules are in excellent agreement with[2] supporting the use of the MP2 method in this work as well as the pseudopotential approach in Ref. 2. The larger contraction for the actinides than for the lanthanides thus appears to be caused mainly by relativistic effects. This importance of the relativistic effects for the actinide contraction was suggested by Bagus *et al.*[35] and demonstrated in atomic calculations by Seth *et al.*[3]

### E. Ligand effects and bonding

The lanthanide and actinide contraction, as measured by orbital radial expectation values, is highly sensitive to the orbital studied. This is demonstrated in Table VI where we present $\langle r \rangle$ values for $(n-1)d$ and $ns$ orbitals of lanthanide and actinide atoms based on average level calculations of $(n-2)f^m(n-1)d^1ns^2$ electronic configurations using the atomic GRASP code.[16] Consequently one would expect the lanthanide and actinide contractions observed at the molecular level to depend on the bonding pattern in the molecular species studied. We obtain at the relativistic MP2 level lanthanide contractions of 0.12, 0.12, and 0.19 Å for the monohydrides, monofluorides, and trihydrides, respectively. The corresponding values for the actinides are 0.20, 0.15, and 0.28 Å. Ligand effects of this type have been observed and discussed in previous studies[2,10] and form the subject of this section. We have performed Mulliken population analysis at the DHF level of the molecular species studied in this work. Although such an analysis has to be approached with some caution, due to basis set sensitivity, the possibility of free rotations among occupied orbitals and also the lack of correlation, it may provide useful information for the understanding of ligand effects. A population analysis for the monohydrides and monofluorides are summarized in Tables VII and VIII.

TABLE VII. Gross Mulliken population analysis of the dominant $\sigma$-type bonding orbital of lanthanide and actinide monohydrides at equilibrium distances. HOMOs is the metal $s$ density in the highest occupied molecular orbital, $Q$ the total metal charge, and $\mu$ the DHF dipole moment in Debye (positive charge on the metal atom).

| | LaH | LuH | AcH | LrH |
|---|---|---|---|---|
| Ms | 0.04 | 0.28 | 0.09 | 0.44 |
| Mp | 0.02 | 0.04 | 0.01 | 0.03 |
| Md | 0.39 | 0.18 | 0.24 | 0.14 |
| Mf | 0.03 | 0.01 | 0.03 | 0.01 |
| Hs | 1.51 | 1.47 | 1.64 | 1.37 |
| HOMOs | 1.56 | 1.44 | 1.64 | 1.32 |
| $Q$ | 0.58 | 0.53 | 0.66 | 0.52 |
| $\mu$ | 1.97 | 1.48 | 2.04 | 2.09 |

For both the monohydrides and monofluorides we find that the highest occupied orbital is essentially a nonbonding metal $ns$ orbital (Tables VII and VIII). This shifts the attention to the metal $(n-1)d$ orbitals for bond formation. The Mulliken population analysis for the bonding orbital in the monohydrides in Table VII do indeed suggest a considerable $d$-contribution to the bonding. This may elucidate the ob-

TABLE VIII. Gross Mulliken population analysis of the three $2p$-like orbitals involved in bonding in lanthanide and actinide monofluorides at equilibrium distances. HOMOs is the metal $s$ density of the highest occupied orbital, $Q$ the total metal charge, and $\mu$ the DHF dipole moment in Debye (positive charge on the metal atom). The Ms occupation is negligible.

| | LaF | LuF | AcF | LrF |
|---|---|---|---|---|
| Mp | 0.18 | 0.04 | 0.27 | 0.06 |
| Md | 0.19 | 0.17 | 0.15 | 0.14 |
| Mf | 0.05 | 0.13 | 0.05 | 0.11 |
| Fp | 5.62 | 5.76 | 5.55 | 5.69 |
| HOMOs | 1.76 | 1.82 | 1.86 | 1.84 |
| $Q$ | 0.81 | 0.85 | 0.76 | 0.86 |
| $\mu$ | 1.50 | 2.15 | 2.04 | 2.98 |

TABLE IX. Gross Mulliken population analysis of the three $\sigma$-type bonding orbitals involved in bonding in lanthanide and actinide trihydrides. $Q$ is the total metal charge.

| | $LaH_3$ | $LuH_3$ | $AcH_3$ | $LrH_3$ |
|---|---|---|---|---|
| Ms | 0.10 | 0.37 | 0.08 | 0.52 |
| Mp | 0.23 | 0.46 | 0.18 | 0.43 |
| Md | 0.89 | 0.66 | 0.67 | 0.66 |
| Mf | 0.08 | 0.03 | 0.07 | 0.04 |
| Hs | 4.70 | 4.44 | 4.99 | 4.31 |
| $Q$ | 1.20 | 1.50 | 0.90 | 1.60 |

served relativistic bond length expansion for these species, since the $(n-1)d$ orbitals undergo a relativistic expansion, as seen from Table VI. Another effect to note in Table VI is that even though both *ns* and $(n-1)d$ orbitals are subject to a contraction due to the imperfect screening of the nuclear charge by the $(n-2)f$ orbitals, the effect is stronger for the *ns* orbitals, so that the $(n-1)d$ and *ns* orbitals are spatially closer to each other at the end of the lanthanide or actinide series, thereby to a larger extent allowing mixing of the orbitals. This effect is especially pronounced in the actinide series. For the monohydrides we accordingly observe that at the beginning of each series metal *d* orbitals are more active in bonding, whereas at the end of the series metal *s* orbitals are more important. This means that the $(n-2)f$ orbitals at the molecular level not only induce orbital contractions, but may change bonding patterns as well. Going from the monohydrides to the monofluorides the bonds become more polar, as witnessed by the increased positive charge on the metal atoms (Table VIII). The fluorine ligand may in a nonrelativistic bonding scheme contribute with $\pi$ orbitals as well as $\sigma$ orbitals. Although the $\pi$ orbitals are largely dominated by fluorine $2p$ orbitals, there are some slight metal contributions on the order of 0.03 electrons, so we will consider all three $2p$-like orbitals in the description of the bonding. It is interesting to note that in both the lanthanide and actinide series, the $\pi$ orbitals are lower than the $\sigma$ orbital in energy, but that this ordering is reversed at the end of both series.

The Mulliken population analysis for the trihydrides are given in Table IX. The molecular point group of the trihydrides is different from that of the linear systems, so we expect a different bonding pattern. In the nonrelativistic $D_{3h}$-symmetry the hydrogen ligands span the irreps $A_1'$ and $E''$. The corresponding symmetry-adapted ligand combinations may interact with *s* and *d* orbitals on the metal atom in $A_1'$ symmetry and with *d* and *f* orbitals in $E''$ symmetry. The doubly degenerate $e''$ orbitals are split by spin–orbit interaction. The spin–orbit splitting is of the order 0.10 and 0.40 eV in the lanthanide and actinide series, respectively. Compared to the monohydride and monofluorides the charge on the metal atom increases from the range 0.52–0.86 electrons to 0.90–1.60 electrons (Table IX). The larger lanthanide and actinide contractions for the trihydrides are presumably connected with the different bonding pattern compared with the monohydrides. Larger *s*-contributions to the bonding in thetrihydrides would explain the larger contractions for the trihydrides since the valence *s* orbitals are contracted more than twice as much as the *d* orbitals. Mulliken population

TABLE X. Dual family basis set for lanthanum. The exponents for the *d* and *f* functions are marked in the *s* and *p* exponent set. The exponent for the Gaussian nucleus is given by $\xi = 1.749\,046\,317\,0 \times 10^8$ (Ref. 24).

| La, *s*, and *p* exponents: | | | |
|---|---|---|---|
| 43 135 364.90 | | 6 205 079.203 | |
| 7 763 487.702 | | 980 045.1863 | |
| 1 814 395.507 | | 214 661.3670 | |
| 496 418.8937 | | 56 772.734 57 | |
| 152 970.2195 | | 17 493.577 53 | |
| 51 816.938 41 | | 6 108.014 156 | |
| 18 986.691 76 | | 2 374.203 128 | |
| 7 381.734 265 | | 1 009.216 460 | |
| 2 999.797 180 | (*d*) | 460.513 644 1 | |
| 1 266.585 320 | (*d*) | 221.662 477 5 | |
| 553.651 006 2 | (*d*) | 110.754 210 8 | |
| 246.956 183 4 | (*d*) | 56.527 194 37 | (*f*) |
| 113.865 160 2 | (*d*) | 28.531 339 56 | |
| 54.250 506 65 | (*d*) | 14.856 578 05 | (*f*) |
| 26.285 252 61 | (*d*) | 7.781 589 308 | (*f*) |
| 12.945 998 06 | (*d*) | 3.855 317 628 | (*f*) |
| 6.292 180 293 | (*d*) | 1.892 802 468 | (*f*) |
| 3.011 157 697 | (*d*) | 0.929 300 000 | (*f*) |
| 1.396 589 864 | (*d*) | 0.456 200 000 | (*f*) |
| 0.647 700 000 | (*d*) | 0.224 000 000 | (*f*) |
| 0.300 400 000 | (*d*) | 0.110 000 000 | |
| 0.139 300 000 | (*d*) | 0.053 990 000 | |
| 0.064 630 000 | (*d*) | 0.026 510 000 | |
| 0.029 970 000 | (*d*) | 0.013 010 000 | |
| 0.013 900 000 | | | |

TABLE XI. Dual family basis set for lutetium. The exponents for the *d* and *f* functions are marked in the *s* and *p* exponent set. The exponent for the Gaussian nucleus is given by $\xi = 1.526\,220\,151\,2 \times 10^8$ (Ref. 24).

| Lu, *s*, and *p* exponents: | | | |
|---|---|---|---|
| 43 379 099.29 | | 9 118 225.456 | |
| 8 343 937.879 | | 1 393 848.900 | |
| 2 044 030.147 | | 302 815.2739 | |
| 568 339.9533 | | 78 743.932 03 | |
| 175 017.9149 | | 23 117.460 42 | |
| 58 488.176 43 | | 7 661.709 706 | |
| 20 944.208 01 | | 2 887.342 975 | |
| 7 948.372 840 | (*d*) | 1 197.417 532 | |
| 3 170.244 625 | (*d*) | 528.227 1001 | |
| 1 320.852 424 | (*d*) | 243.130 7216 | (*f*) |
| 571.193 9175 | (*d*) | 115.465 8230 | (*f*) |
| 250.605 5893 | (*d*) | 57.732 911 50 | (*f*) |
| 115.565 1092 | (*d*) | 28.866 455 75 | (*f*) |
| 54.807 591 08 | (*d*) | 14.433 227 88 | (*f*) |
| 26.602 806 33 | (*d*) | 7.216 613 940 | (*f*) |
| 12.859 967 41 | (*d*) | 3.546 250 000 | (*f*) |
| 6.065 673 500 | (*d*) | 1.742 630 000 | (*f*) |
| 2.861 000 000 | (*d*) | 0.856 328 000 | (*f*) |
| 1.349 450 000 | (*d*) | 0.420 800 000 | (*f*) |
| 0.636 497 000 | (*d*) | 0.206 781 000 | (*f*) |
| 0.300 217 000 | (*d*) | 0.101 612 000 | |
| 0.141 604 000 | (*d*) | 0.049 932 400 | |
| 0.066 790 400 | (*d*) | 0.024 536 800 | |
| 0.031 503 100 | (*d*) | 0.012 057 400 | |
| 0.014 859 100 | | | |

TABLE XII. Dual family basis set for actinium. The exponents for the *d* and *f* functions are marked in the *s* and *p* exponent set. The exponent for the Gaussian nucleus is given by $\xi = 1.306\,673\,097\,4 \times 10^8$ (Ref. 24).

| Ac, *s*, and *p* exponents: | | | |
|---|---|---|---|
| 345 000 000.0 | | 23 770 799.38 | |
| 115 000 000.0 | | 4 792 928.272 | |
| 38 300 000.00 | | 1 171 896.044 | |
| 12 800 000.00 | | 324 477.3750 | |
| 4 250 000.000 | | 98 972.693 06 | |
| 1 427 545.073 | | 32 810.823 09 | |
| 511 837.5804 | | 11 767.737 76 | |
| 192 367.7760 | | 4 556.295 110 | |
| 75 320.133 66 | | 1 893.147 174 | |
| 30 398.157 64 | | 835.147 666 2 | (*f*) |
| 12 540.136 65 | (*d*) | 386.447 355 2 | (*f*) |
| 5 282.976 541 | (*d*) | 185.532 997 3 | (*f*) |
| 2 284.306 815 | (*d*) | 90.071 598 63 | (*f*) |
| 1 016.515 311 | (*d*) | 45.477 781 71 | (*f*) |
| 463.787 490 2 | (*d*) | 22.889 039 49 | (*f*) |
| 219.596 153 9 | (*d*) | 11.442 776 70 | (*f*) |
| 107.300 800 5 | (*d*) | 5.690 993 203 | (*f*) |
| 53.882 934 70 | (*d*) | 2.710 000 000 | (*f*) |
| 27.329 378 88 | (*d*) | 1.290 500 000 | (*f*) |
| 13.708 176 43 | (*d*) | 0.614 510 000 | (*f*) |
| 6.868 652 342 | (*d*) | 0.292 620 000 | (*f*) |
| 3.219 583 579 | (*d*) | 0.139 340 000 | |
| 1.499 913 474 | (*d*) | 0.066 355 000 | |
| 0.697 630 000 | (*d*) | 0.031 598 000 | |
| 0.324 480 000 | (*d*) | 0.015 046 000 | |
| 0.150 920 000 | (*d*) | | |
| 0.070 196 000 | (*d*) | | |
| 0.032 649 000 | (*d*) | | |
| 0.015 186 000 | | | |

TABLE XIII. Dual family basis set for lawrencium. The exponents for the *d* and *f* functions are marked in the *s* and *p* exponent set. The exponent for the Gaussian nucleus is given by $\xi = 1.198\,768\,319\,1 \times 10^8$ (Ref. 24).

| Lr, *s*, and *p* exponents: | | | |
|---|---|---|---|
| 385 000 000.0 | | 28 914 065.75 | |
| 128 000 000.0 | | 6 386 780.132 | |
| 42 800 000.00 | | 1 646 282.264 | |
| 14 276 833.09 | | 469 969.1413 | |
| 4 749 869.527 | | 145 296.7628 | |
| 1 721 784.705 | | 48 101.307 20 | |
| 667 162.3754 | | 16 990.040 79 | |
| 267 973.7341 | | 6 407.641 882 | |
| 110 568.3958 | | 2 579.073 957 | |
| 46 132.326 51 | | 1 101.339 032 | (*f*) |
| 19 285.551 62 | (*d*) | 494.540 021 1 | (*f*) |
| 8 103.690 008 | (*d*) | 231.318 717 8 | (*f*) |
| 3 462.812 086 | (*d*) | 109.578 288 4 | (*f*) |
| 1 517.064 720 | (*d*) | 53.942 926 99 | (*f*) |
| 681.181 753 1 | (*d*) | 26.708 277 21 | (*f*) |
| 318.970 967 6 | (*d*) | 13.274 980 86 | (*f*) |
| 155.104 855 1 | (*d*) | 6.380 909 850 | (*f*) |
| 77.737 932 99 | (*d*) | 3.067 750 000 | (*f*) |
| 39.348 411 36 | (*d*) | 1.474 880 000 | (*f*) |
| 19.948 908 08 | (*d*) | 0.709 076 000 | (*f*) |
| 10.207 215 34 | (*d*) | 0.340 902 000 | (*f*) |
| 4.951 246 244 | (*d*) | 0.163 895 000 | (*f*) |
| 2.335 490 000 | (*d*) | 0.078 795 700 | |
| 1.101 650 000 | (*d*) | 0.037 882 600 | |
| 0.519 645 000 | (*d*) | 0.018 212 800 | |
| 0.245 116 000 | (*d*) | | |
| 0.115 620 000 | (*d*) | | |
| 0.054 538 000 | (*d*) | | |
| 0.025 725 400 | (*d*) | | |
| 0.012 134 700 | | | |

analysis does not support this explanation, however, because there is less *s*-character in each bond in the trihydrides than there is in the monohydrides. The differences are small though and may be an artefact of the Mulliken analysis method (Table VI).

Given the fact that the *s* and *d* orbitals are spatially closer at the end of the *f*-block an increased *s*-participation in the bonding for the late compared to the early *f*-elements seems probable. For the monohydrides the Mulliken analysis shows unambiguously that the bonding has large *d* (small *s*) contributions for the early *f*-elements and large *s* (small *d*) contributions for the late *f*-elements. For the trihydrides there is a much larger $s/d$-ratio at the end of the *f*-block, but for the fluorides the evidence is less convincing. It is well known that *s* orbitals are contracted by relativity whereas *d* orbitals are expanded by indirect relativistic effects as is also seen from Table VI. Indeed we observe that the relativistic bond expansion is larger for lanthanum and actinium at the beginning of the *f*-block compared with lutetium and actinium for all the molecules in this study.

Wang and Schwarz[10] attributes ligand effects in the monosubstituted compounds to two factors: The participation of unfilled $4f$ orbitals and the ''rigidity'' of the bond. The importance of the former factor is displayed by calculations on LaH by Dolg and Stoll.[8] Pseudopotential CI calculations with the $4f$ population fixed to zero gives a bond length of 2.09 Å. When a variable $4f$ occupation is allowed for, the bond length is reduced to 2.01 Å. At the DHF level the total *f*-contribution to LaH is 0.03 electrons, of which effectively *all* is located to the bonding orbital. This strongly suggests that *f* functions are needed in the basis for polarization of the bonding $5d$ orbitals. Indeed, without sufficiently tight *f* functions in the basis our DHF calculations at first go converge to an excited $\sigma^2\delta^2$ state instead of the $\sigma_1^2\sigma_2^2$ ground state. In LaF and $LaH_3$ the total *f* contribution is 0.05 and 0.08 electrons, respectively, restricted to bonding orbitals. For the analogous molecular species of actinum the *f* contributions to bonding orbitals is 0.03, 0.05, and 0.07 electrons, respectively. It may be better not to attribute the *f* contribution to $4f$ or $5f$ orbitals specifically since this gives the impression of a backbonding effect. With significant metal *d* contribution to bonding, the *f* functions are needed for polarization, as is well known for other systems.

Wang and Schwarz[10] also correlate lanthanide contraction and bond rigidity, which may be represented by the average force constant. For lanthanide monohydrides, monofluorides, and monooxides, representing a transition from soft to rigid bonds, they calculated contractions of 0.19, 0.12, and 0.06 Å, respectively. We have only calculated lanthanide contraction for the first two members of this series, but at the relativistic MP2 level we get almost identical values for the monohydrides (0.123 Å) and monofluorides (0.122 Å), thus making this trend less obvious. A further problem with the analysis of Wang and Schwarz is that part

of their motivation was based on a experimental bond length of LaH of 2.10 Å, based on a $^3\Delta$ ground state. The recent spectroscopic work of Ram and Bernath[28] shows a $^1\Sigma^+$ ground state of LaH with an equilibrium bond length of 2.032 Å, in close agreement with our results. Thereby the experimental lanthanide contraction for the series LnX (X=H, F, O) becomes 0.120, 0.109, and 0.036 Å, indicating that perhaps further studies are necessary for a complete understanding of ligand effects. On the other hand, for the actinide compounds studied in this work we do have a correlation between the bond rigidity and the actinide contraction.

## IV. CONCLUSION

We have performed a study of the molecular contraction for the lanthanide and actinide monohydrides, trihydrides, and monofluorides with the DIRAC DHF program[11] and the recently developed direct RMP2 module. Between 10% and 30% of the calculated molecular lanthanide contractions are caused by relativity. The actinide contraction is larger than the lanthanide contraction for all the three types of molecules that we have studied. This is a consequence of relativity.

Large basis sets have been employed with between 869 and 1218 scalar Cartesian basis functions used in the expansion of the wave functions. These calculations are feasible mainly due to the sophisticated direct SCF and integral screening techniques built into the DIRAC program. With these developments the four-component calculations are no longer prohibitively expensive compared to standard nonrelativistic calculations. Due to the requirements of the kinetic balance condition the scalar basis sets in the DHF calculations are more than twice the size of the sets for the HF calculations. However, the fully relativistic four-component SCF calculations are not more than a factor of 5–11 more expensive than the nonrelativistic calculations for the molecules we have studied. The cost of the RMP2 calculations in this study where the $(SS|SS)$ integrals are not included in the MP2 energy expression, is equivalent to the cost of between five and seven DHF iterations. Fully relativistic MP2 calculations with a considerable number of correlated electrons may, therefore, be performed at a fraction of the cost of the DHF calculations. Inclusion of the $(SS|SS)$ integrals increases the time by about a factor of 2.5, but has a negligible effect on the spectroscopic constants we have studied, as shown in this work and in Ref. 15.

Earlier four-component relativistic calculations have frequently focused on a single molecule or a vertical trend in the periodic system where the relativistic effects have been of importance in perhaps one or two of the systems studied. This is one of the first fully relativistic studies for a class of molecules where trends have been followed both vertically *and* horizontally in the periodic system for a number of systems with significant relativistic effects. We have demonstrated that it is possible to perform these correlated investigations of trends in the periodic system without the possible errors that are introduced when less rigorous approximations are invoked to account for the effect of relativity. By comparing our results with earlier quasirelativistic pseudopotential calculations we have also been able to demonstrate that the MP2 method gives reasonably accurate results for these compounds compared with a more sophisticated treatment of correlation. Finally we have demonstrated that while approximate treatments of relativity might yield excellent results for some systems, the fully relativistic calculations are extremely valuable in benchmark calibrations of more approximate methods.

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## APPENDIX: BASIS SET OPTIMIZATION

Lanthanum. A $23s20p14d$ dual family basis set was optimized, and the four (three) outer $s$ ($p$) functions were replaced by an even-tempered series of six (seven) functions. Two diffuse $d$ functions were also added. Numerical experiments on LaH showed that is was necessary to add eight polarization $f$ functions to obtain an accurate description of the bonding. The final $25s24p16d8f$ basis set is given in Table X. The average of configuration DHF energy for the $[\mathrm{Xe}]6s^25d^1$ configuration of the atom is $3.82\times10^{-3}$ a.u. above the finite difference result from GRASP[16,24] which we regard as the DHF limit.

Lutetium. A $23s20p14d9f$ dual family basis set was optimized, and the six (five) outer $s$ ($p$) functions were replaced by an even-tempered series of eight (nine) functions. Three (two) diffuse functions were added to the $d$ ($f$) function set. The final $25s24p17d11f$ basis set is given in Table XI. The average of configuration energy for the $[\mathrm{Xe}]4f^{14}6s^25d^1$ configuration of the atom is $16.01\times10^{-3}$ a.u. above the DHF limit.[24]

Actinium. A $26s21p16d9f$ dual family basis set was optimized, and the inner four $s$ functions were replaced by an even-tempered series of five functions. The four (four) outer $s$ ($p$) functions were replaced by an even-tempered series of six (eight) functions. Two (three) diffuse $d$ ($f$) functions were also added in the final $29s25p18d12f$ basis set. The basis set is given in Table XII. The average of configuration energy for the $[\mathrm{Rn}]7s^26d^1$ configuration is $15.18\times10^{-3}$ a.u. above the DHF limit.[24]

Lawrencium. A $25s21p16d11f$ dual family basis set was optimized, and the inner $s$ function were replaced by an even-tempered series of three functions. The five (four) outer $s$ ($p$) functions were replaced by an even-tempered series of eight (eight) functions. Three (two) diffuse $d$ ($f$) functions were also added in the final $30s25p19d13f$ basis set. The basis set is given in Table XIII. The average of configuration energy for the $[\mathrm{Rn}]4f^{14}7s^26d^1$ configuration is $43.81\times10^{-3}$ a.u. above the DHF limit.[24]

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